Supporting Information

Halogen Bonding Aza-BODIPYs for Anion Sensing and Anion Binding-Modulated Singlet Oxygen Generation

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1. Instrumentation and General Experimental Details

General Information

Solvents and reagents were purchased from commercial suppliers and used as received. Dry solvents were obtained by purging with nitrogen and passing through a MBraun MPSP-800 column. H_2O was de-ionised and micro-filtered using a Milli-Q® Millipore machine.

Experiments were conducted at room temperature unless otherwise stated. Merck silica gel 60 was used for flash column chromatography. TBA salts were stored in vacuum desiccators prior to use. NMR spectra were either recorded on a Bruker Avance III HD Nanobay NMR spectrometer equipped with a 9.4 T magnet or a Bruker NEO 600 with broadband helium cryoprobe. ^{1}H NMR titrations were recorded on a Bruker Avance III NMR equipped with a 11.75 T magnet.

Chemical shifts are quoted in parts per million relative to the residual solvent peak.

UV-vis and fluorescence measurements were carried out on a Duetta (Horiba) using quartz cuvettes with a path length of 10 mm. Fluorescence spectra were acquired with a wavelength of excitation of 600 for receptor **1**, and 615 nm for receptor **2** nm, 5 nm excitation and emission slits and were recorded in, at least, triplicate repeat measurements to ensure signal stability. Anion titration studies were carried out by titrating a 1 μM solution of the receptor with aliquots of a concentrated solution of TBA-anion in the same receptor solution to ensure a constant receptor concentration.

Photo-irradiation of samples for singlet oxygen experiments was accomplished using a Thorlabs mounted LED (model M625L4), mounted in a custom set-up directly above the cuvette containing the liquid sample.

Fluorescence lifetimes were measured on an Edinburgh Instruments FS5 spectrofluorometer operating Fluoracle® software, using in time-correlated single photon counting (TCSPC) mode using a picosecond pulsed diode laser (EPL-475) as the excitation source. The detector was a R13456 PMT detector (200–950 nm spectral coverage, Hamamatsu). Measurements were conducted at 298 K.

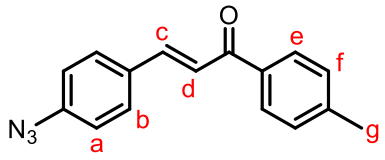
Spectroscopic grade acetone (Alfa Aesar) was used throughout.

Tris[(1-benzyl-1H-1,2,3-triazol-4-yl)methyl]amine is abbreviated as TBTA.

All data analysis and fitting were carried out with *OriginPro* 2023.[1]

2. Synthesis and Characterisation of Compounds

Compound 3B



4-azidobenzaldehyde[2] (1.3g, 8.84mmol) and 4-methylacetophenone (1.16mL, 8.84mL) were dissolved in ethanol (10mL) and cooled to 0°C. 2.5mL of 50% (w/w) aqueous KOH was added and the mixture left to stir overnight in the dark. The solution was neutralized with HCl and diluted with H_2O (20mL), then filtered. The solid was recrystallized from EtOH to yield compound **3B** as a yellow solid (1.7g, 73%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 – 7.90 (m, $2H_e$), 7.77 (d, *J* = 15.7 Hz, $1H_c$), 7.68 – 7.60 (m, $2H_b$), 7.49 (d, *J* = 15.7 Hz, $1H_d$), 7.34 – 7.28 (m, $2H_f$), 7.11 – 7.03 (m, $2H_a$), 2.44 (s, $3H_g$).

^{13}C NMR (101 MHz, $CDCl_3$) δ 189.81, 143.72, 143.19, 142.07, 135.62, 131.86, 129.98, 129.37, 128.64, 121.59, 119.55, 21.70.

HRMS (ESI +ve) m/z: 264.1132, ($[M+H]^+$, $C_{16}H_{14}ON_3$ requires 264.1131).

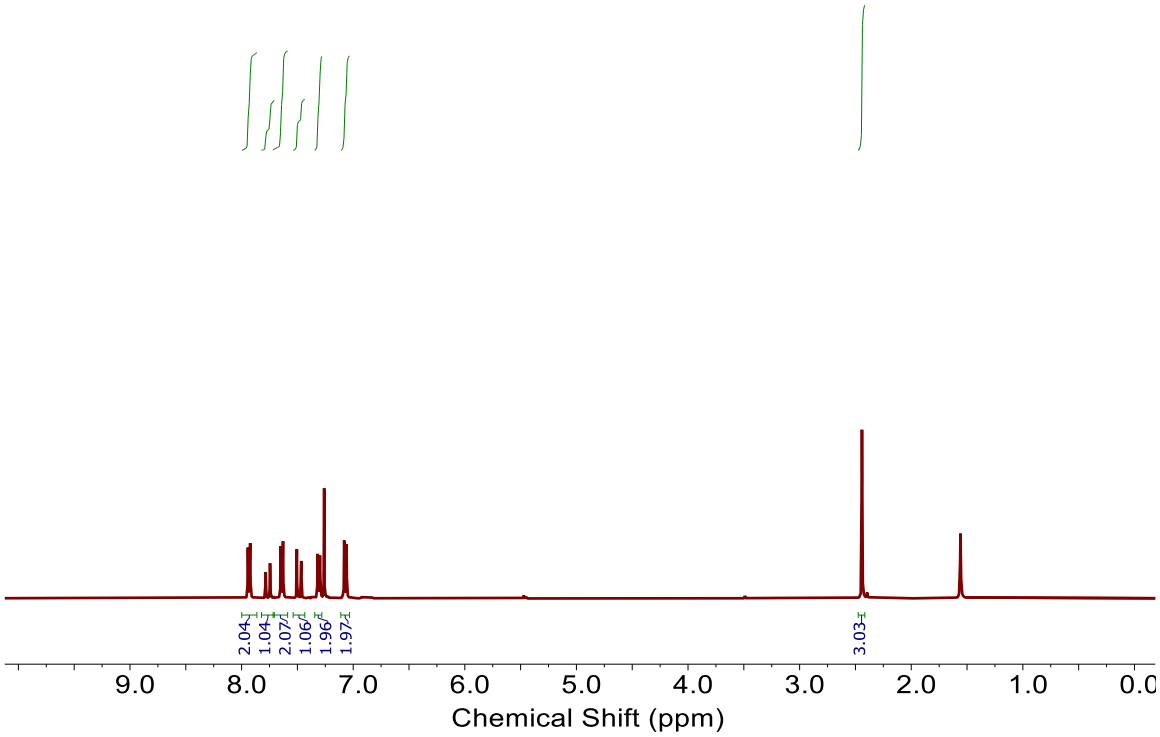


Figure S1. ^{1}H NMR spectrum of **3B.**

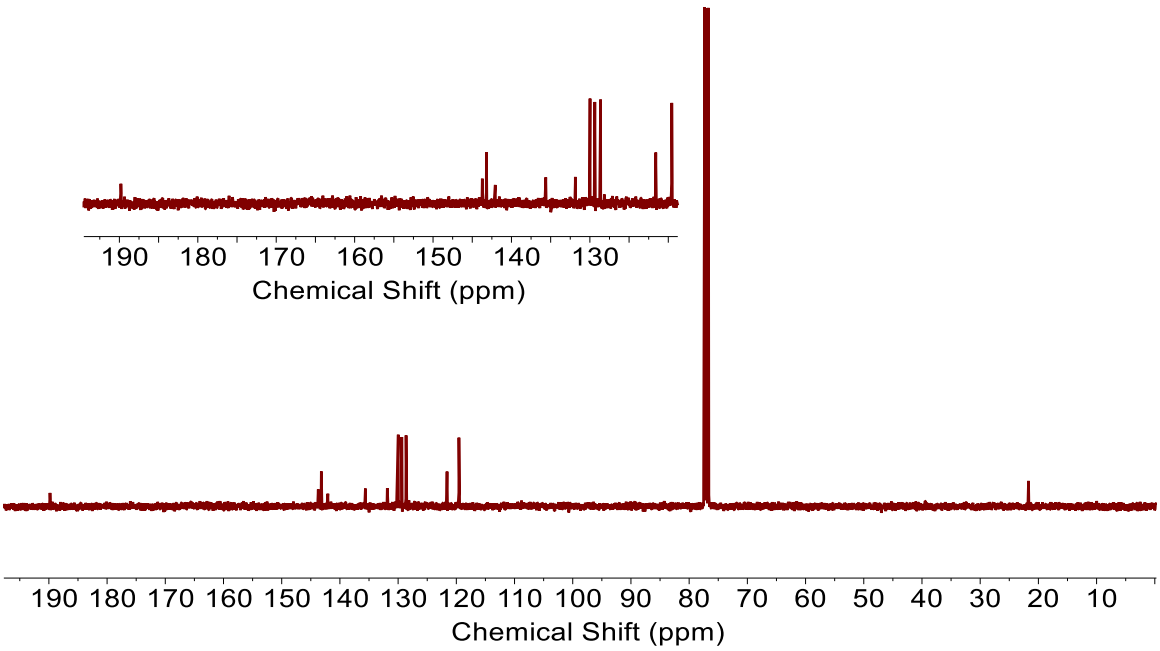


Figure S2. ^{13}C NMR spectrum of **3B.**

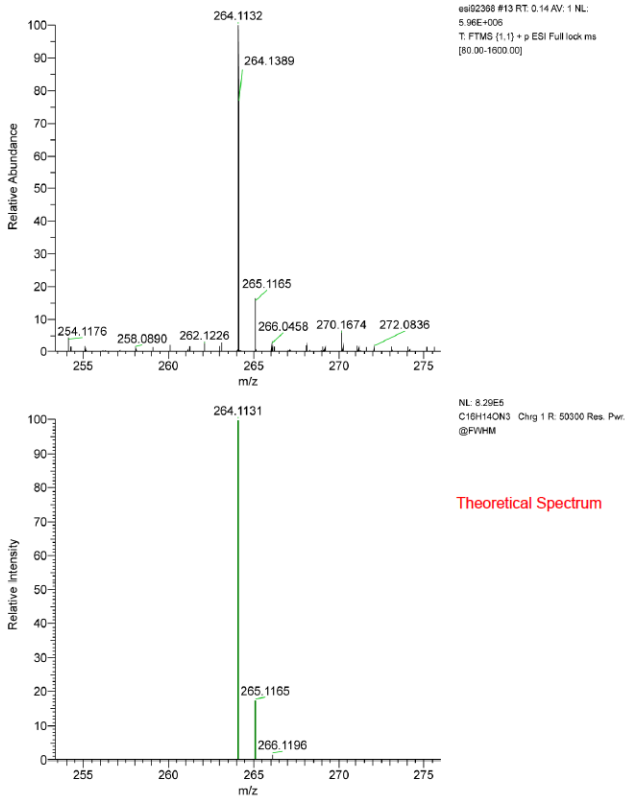
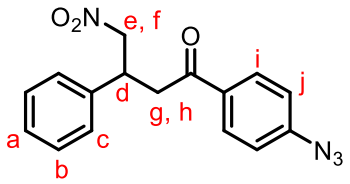


Figure S3. Experimental and theoretical mass spectra of **3B.**

Compound 4A



Compound **3A**[3] (1.29g, 5.18mmol), $MeNO_2$ (1.4mL, 26mmol) and TEA (1mL) were dissolved in EtOH (5mL) and the mixture stirred at reflux overnight. The reaction mixture was allowed to cool, and then was acidified with HCl (2M) and diluted with distilled H_2O (10mL). The aqueous mixture was extracted with EtOAc (3x15mL) and the combined organic layers were dried over $MgSO_4$ and filtered. The solvent was removed *in vacuo* to give the crude product, which was purified by flash column chromatography (Hex:EtOAc 85:15 (*v/v*)). Compound **4A** was isolated as thick yellow oil (1.14g, 71%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 – 7.88 (m, $2H_i$), 7.38 – 7.26 (m, $5H_{a,b,c}$), 7.09 – 7.05 (m, $2H_j$), 4.83 (dd, J = 12.5, 6.7 Hz, $1H_e$), 4.69 (dd, J = 12.5, 7.8 Hz, $1H_f$), 4.21 (m, $1H_d$), 3.50 – 3.34 (m, $2H_{g,h}$).

^{13}C NMR (101 MHz, $CDCl_3$) δ 195.42, 145.59, 139.17, 133.15, 130.16, 129.26, 128.09, 127.59, 119.27, 79.69, 41.51, 39.48.

HRMS (ESI +ve) m/z: 333.0955, ($[M+Na]^+$, $C_{16}H_{14}O_3N_4Na$ requires 333.0958).

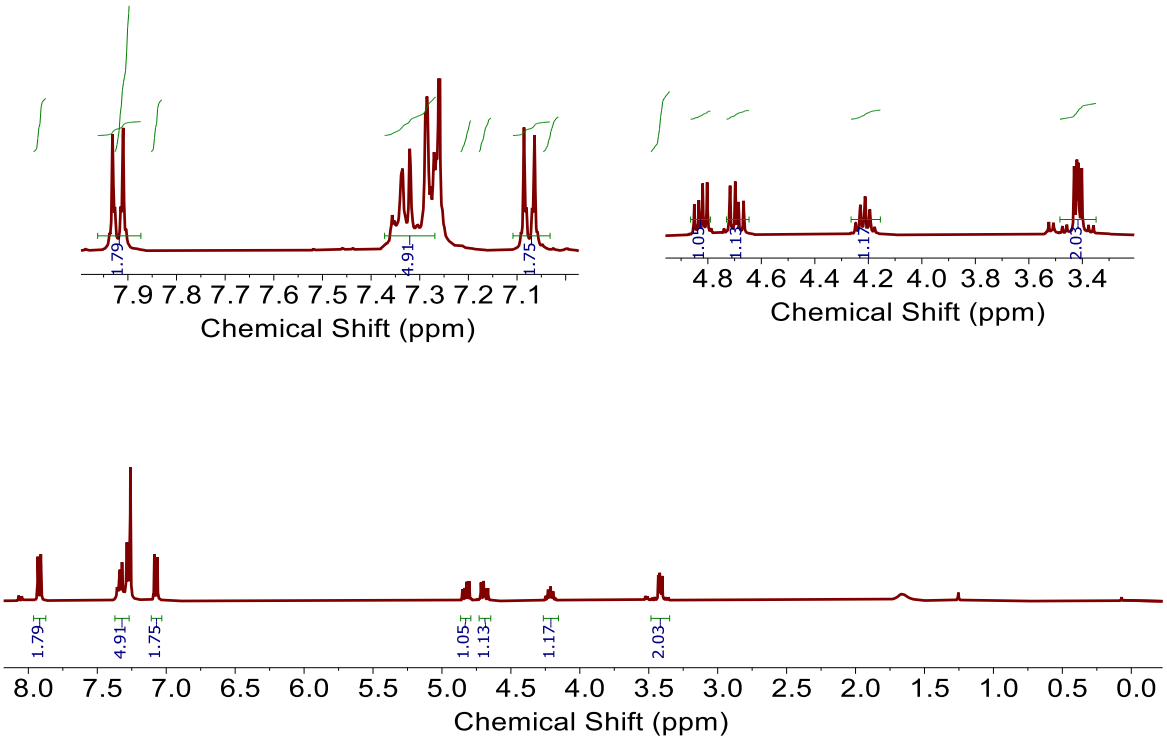


Figure S4. ^{1}H NMR spectrum of **4A.**

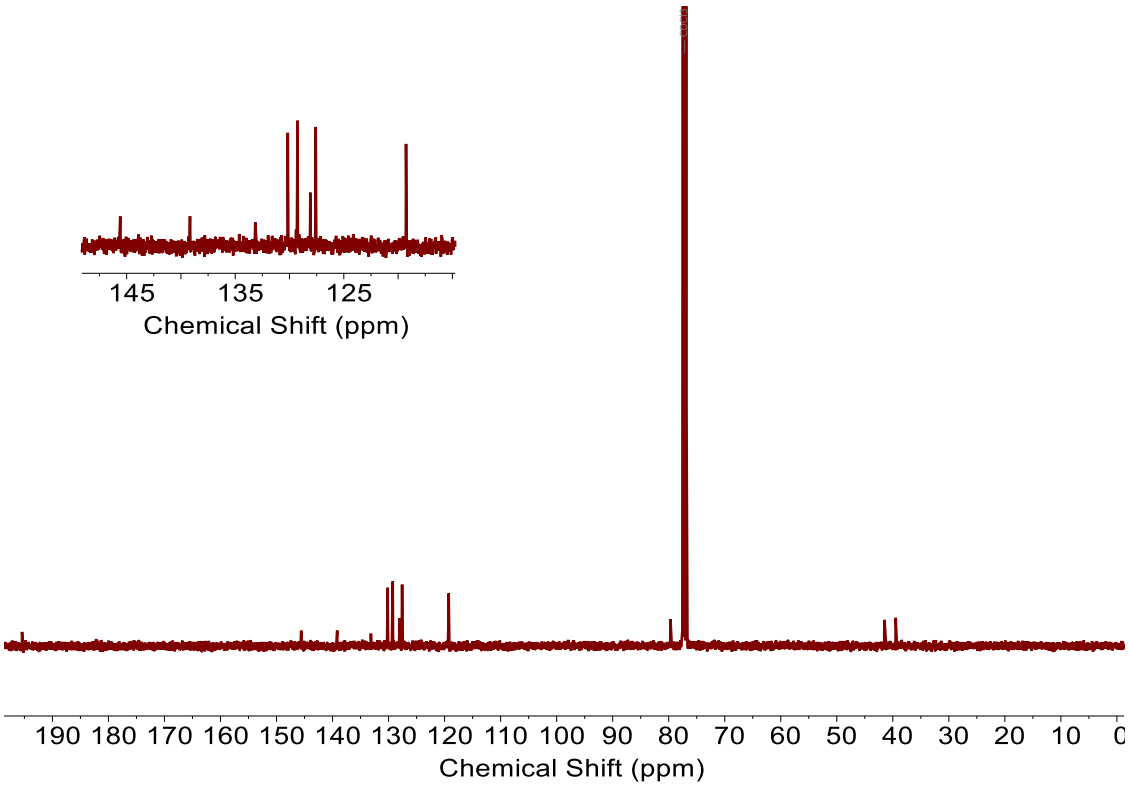


Figure S5. ^{13}C NMR spectrum of **4A.**

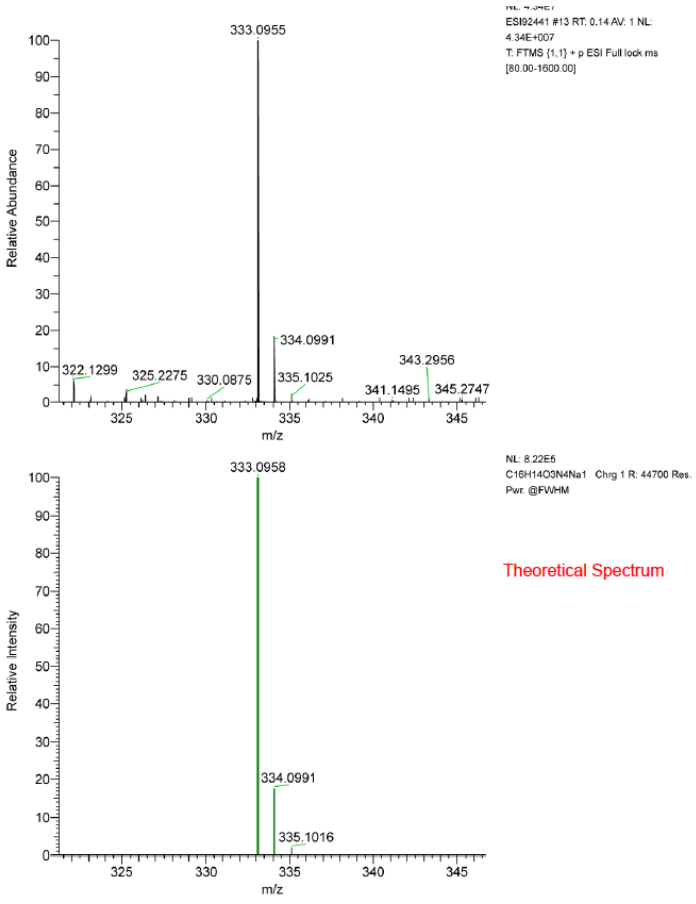
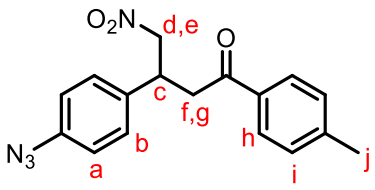


Figure S6. Experimental and theoretical mass spectra of **4A.**

Compound 4B



Compound **3B** (1.7g, 6.46mmol), triethylamine (4.5mL, 32.31mmol) and nitromethane (1.75mL, 32.31mmol) were dissolved in EtOH (75mL) and heated at reflux overnight. The solution was allowed to cool, and the solvent removed *in vacuo*. The residue was dissolved in DCM (50mL) and washed with 1M HCl (20mL) and brine (2x20mL). The organic layer was dried over $MgSO_4$ and filtered, and the solvent was removed *in vacuo*. The crude mixture was purified by flash column chromatography (85:15 Hex:EtOAc (*v/v*)) to yield compound **4B** as a thick orange oil (1.3g, 62%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 – 7.75 (m, $2H_h$), 7.29 – 7.22 (obscured by residual solvent peak) (m, $4H_{a,b}$), 7.01 – 6.95 (m, $2H_i$), 4.81 (dd, J = 12.5, 6.4 Hz, $1H_d$), 4.65 (dd, J = 12.5, 8.2 Hz, $1H_e$), 4.20 (m, $1H_c$), 3.48 – 3.32 (m, $2H_{f,g}$), 2.41 (s, $3H_j$).

^{13}C NMR (101 MHz, $CDCl_3$) δ 196.35, 144.79, 139.78, 135.95, 133.98, 129.61, 129.09, 128.28, 119.78, 79.70, 41.41, 38.97, 21.83.

HRMS (ESI +ve) m/z: 347.1114, ($[M+Na]^+$, $C_{17}H_{16}O_3N_4Na$ requires 347.1115).

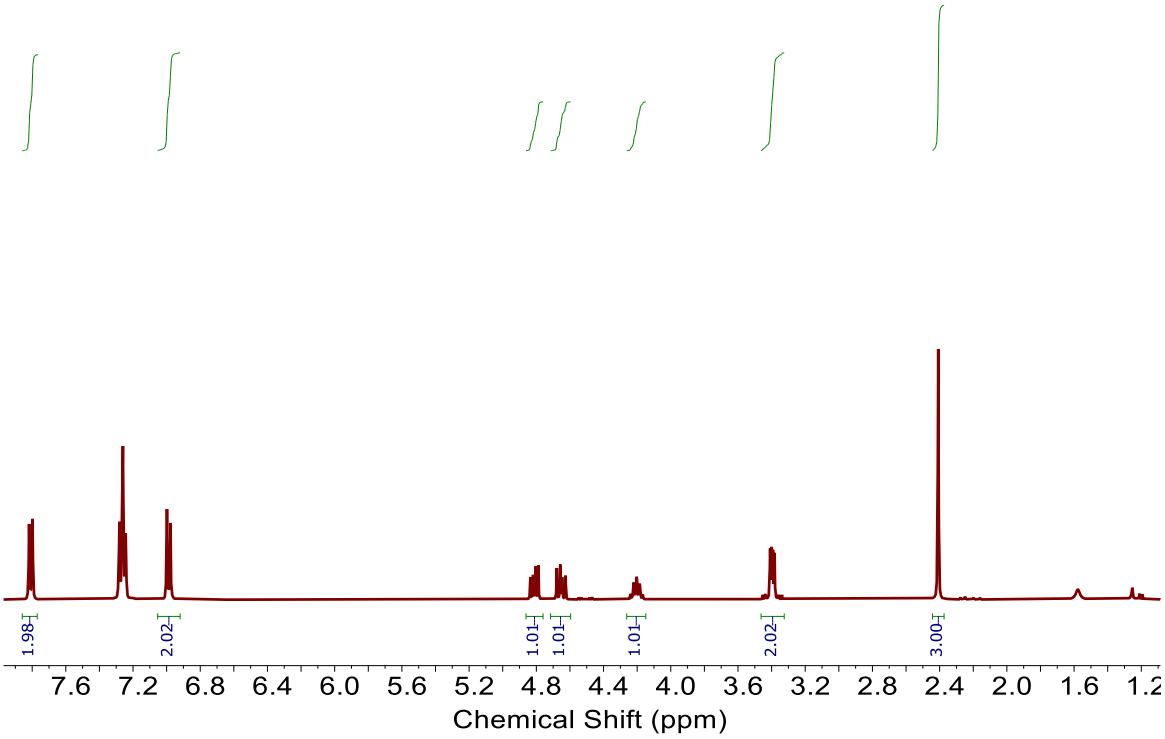


Figure S7. ^{1}H NMR spectrum of **4B.**

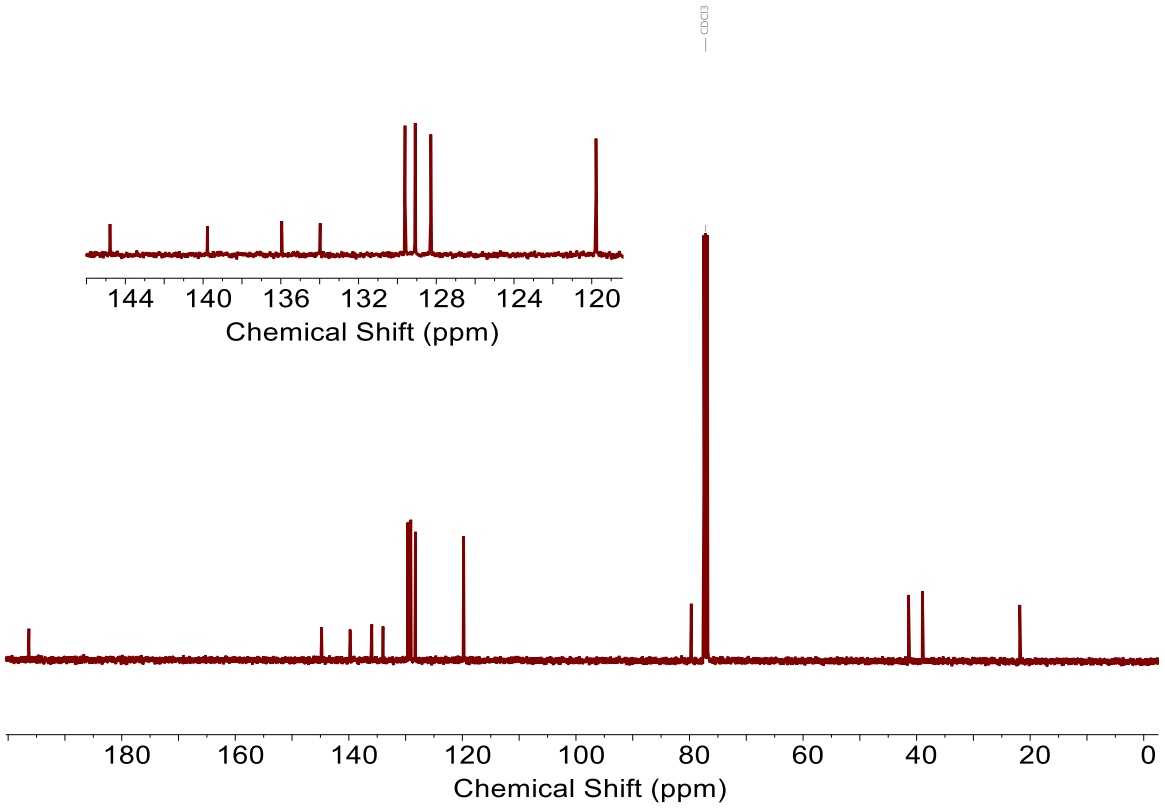


Figure S8. ^{13}C NMR spectrum of **4B.**

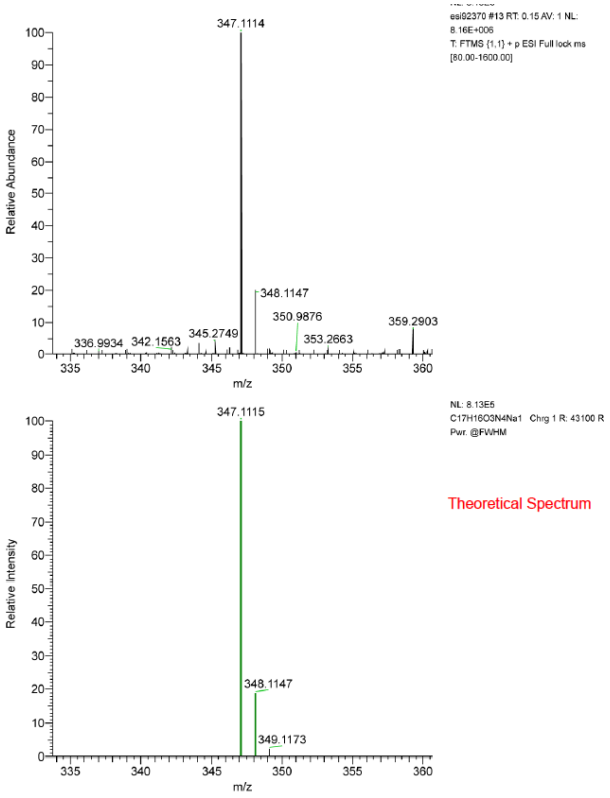
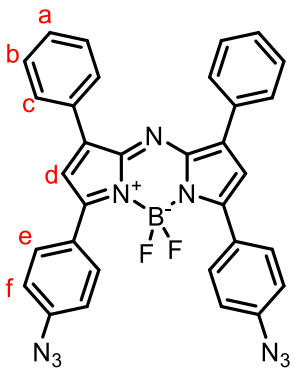


Figure S9. Experimental and theoretical mass spectra of **4B.**

Compound 6A



Compound **6A** was prepared via a modified literature procedure.[4] Compound **4A** (300mg, 0.97mmol) and NH_4OAc (2.61g, 34mmol) were suspended in n-BuOH (7mL) and stirred at 120°C for 24h. The solution was cooled to 0°C and diluted with hexane (7mL). The solution was filtered, and the solid washed with water and minimum cold EtOH to yield intermediate 5A as a blue solid. Without further purification, the intermediate **5A** was dissolved in dry DCM (15mL) and treated with triethylamine (0.52mL, 3.7mmol) and $BF_3{\cdot}OEt_2$ (0.64mL, 5.18mmol)

and stirred under N_2 overnight. The reaction mixture was then diluted with DCM (50mL) and washed with water (3x20mL) and 1M NaOH (20mL). The organic layer was dried over $MgSO_4$, filtered and the solvent removed *in vacuo*. The crude product was purified by flash column chromatography (40:40:20 DCM:Hex:Toluene (*v/v*)) to yield compound **6A** as a green solid (50mg, 18%, two steps).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 – 8.02 (m, 8$H_{e,f}$), 7.47 (m, 6$H_{a,b}$), 7.21 – 7.11 (m, 4H_c), 7.05 (s, 2H_d).

^{13}C NMR (151 MHz, $CDCl_3$) δ 158.12, 145.85, 144.25, 142.96, 132.36, 131.54, 129.74, 129.52, 128.81, 128.26, 119.50, 118.99.

^{19}F NMR (377 MHz, $CDCl_3$) δ -130.99 – -132.15 (m).

^{11}B NMR (128 MHz, $CDCl_3$) δ 0.88 (t, J = 36.6 Hz).

HRMS (ESI +ve) m/z: 580.1972, ($[M+H]^+$, $C_{32}H_{21}N_9BF_2$ requires 580.1979).

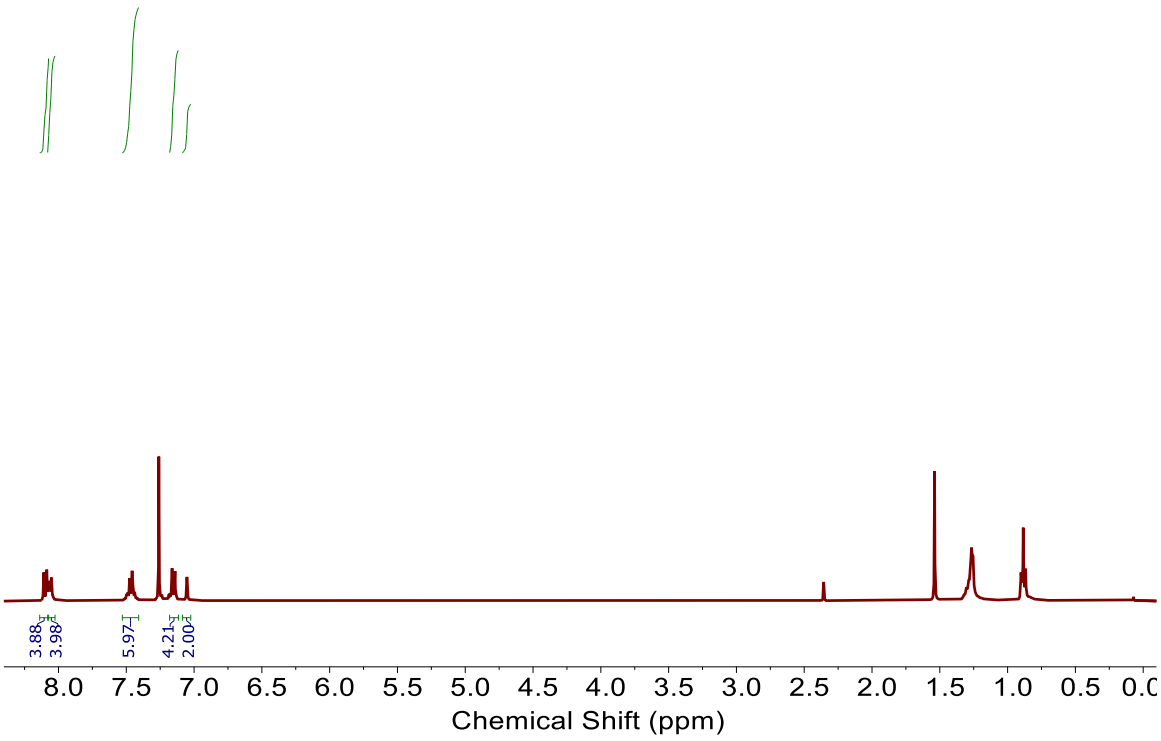


Figure S10. ^{1}H NMR spectrum of **6A.**

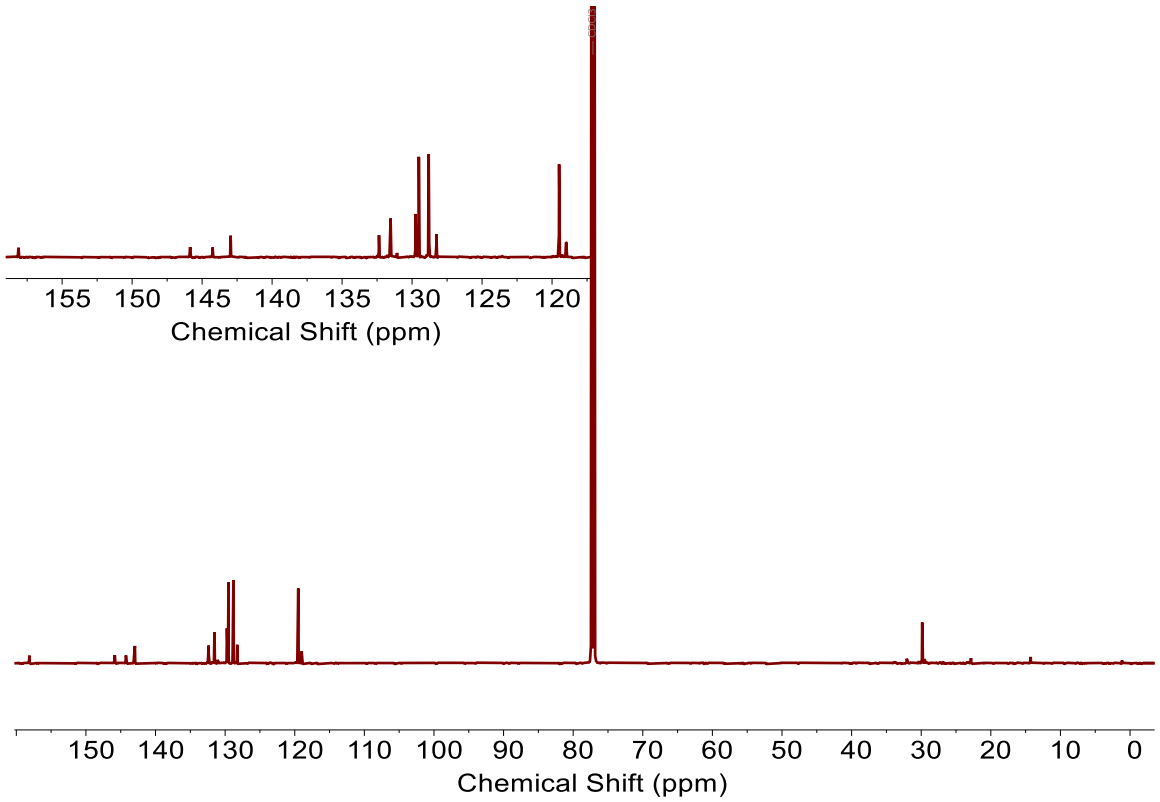


Figure S11. ^{13}C NMR spectrum of **6A.**

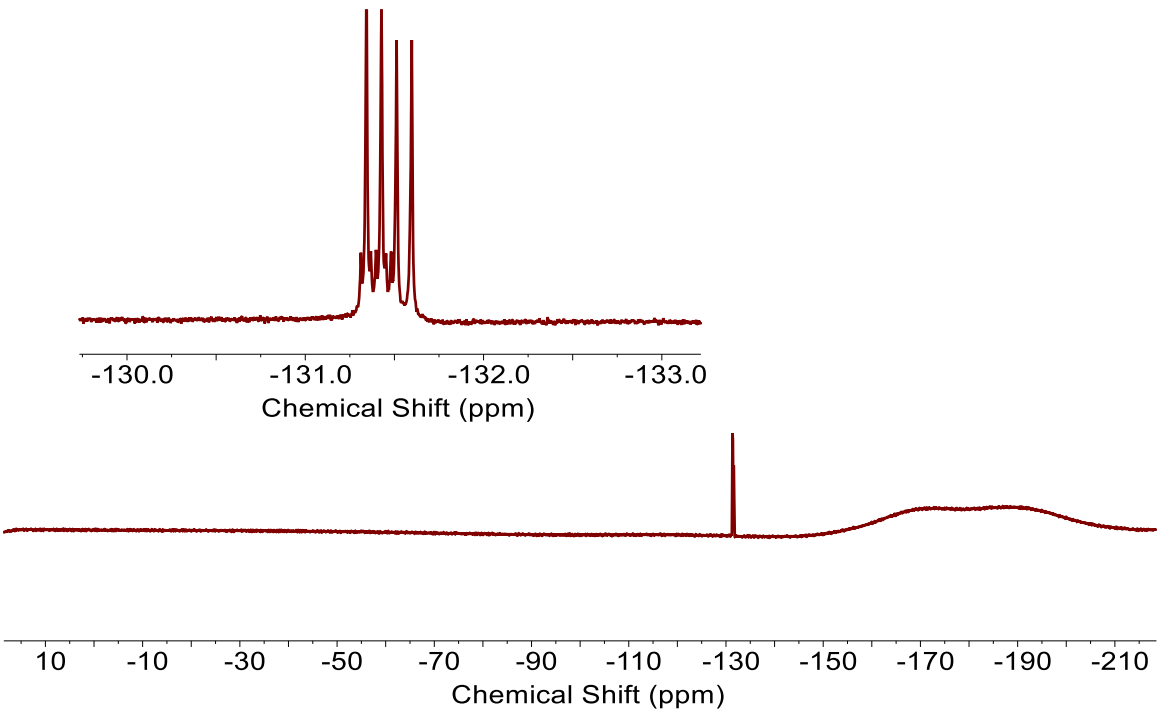


Figure S12. ^{19}F NMR spectrum of **6A.**

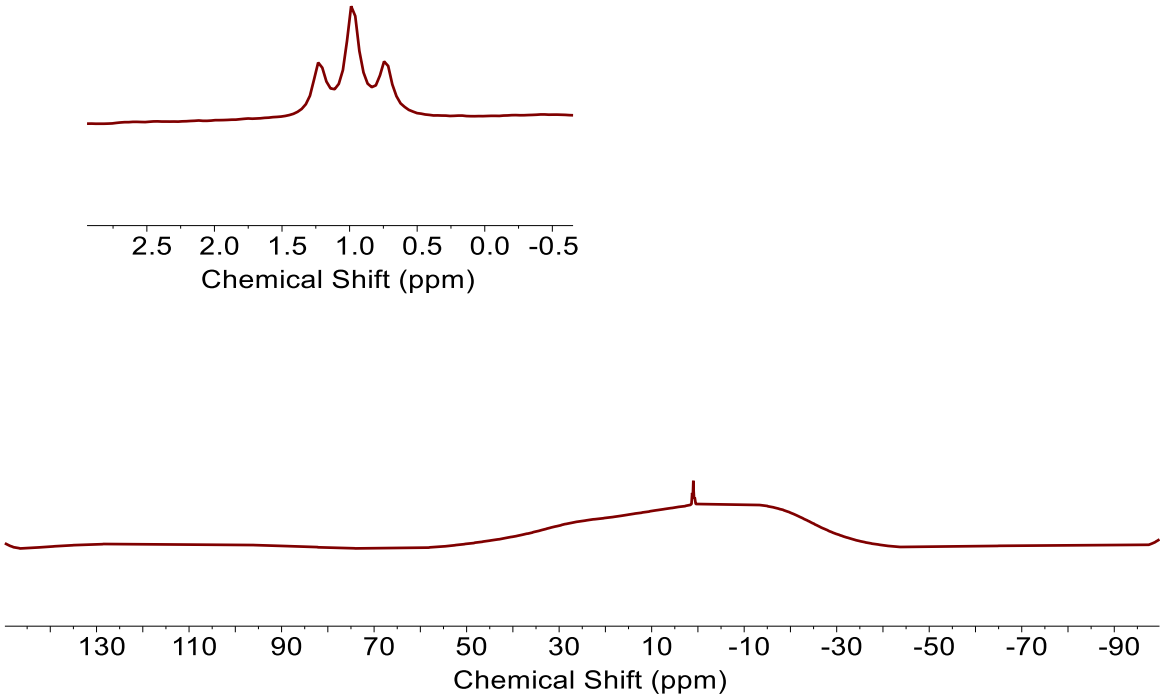


Figure S13. ^{11}B NMR spectrum of **6A.**

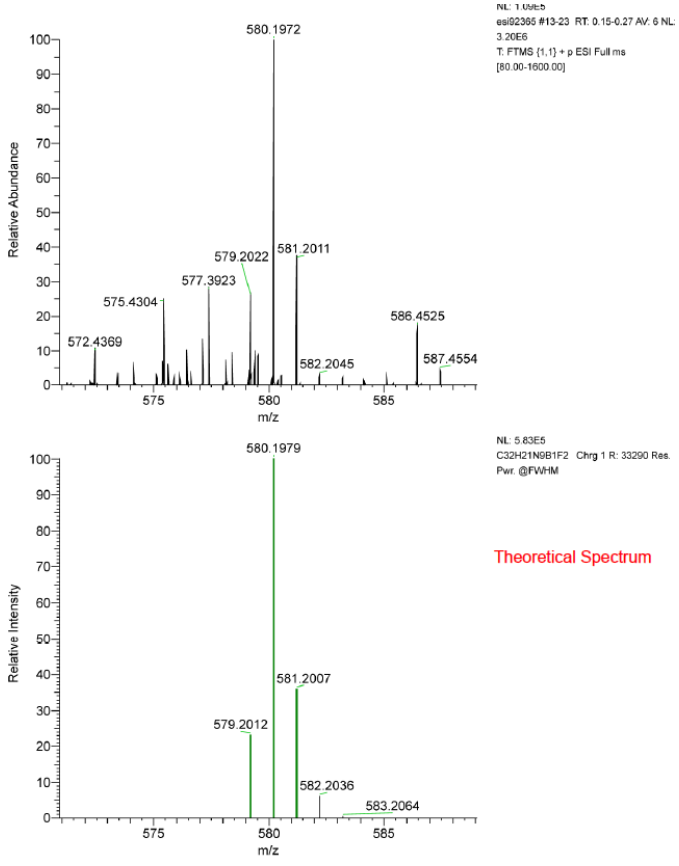
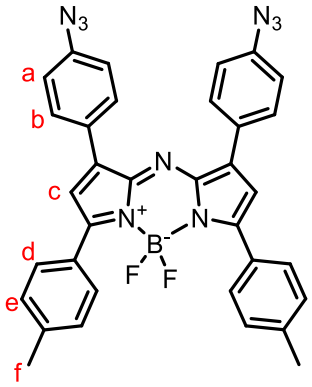


Figure S14. Experimental and theoretical mass spectra of **6A.**

Compound 6B



Compound **4B** (750mg, 2.31mmol) was dissolved in n-BuOH (18mL) and NH_4OAc (4.45g, 58mmol) was added. The suspension was heated at reflux for 24h and then allowed to cool. The solution was diluted with hexane (5mL), cooled to 0°C and filtered. The solid was washed with water and minimum cold ethanol to yield intermediate **5B** as a blue solid. Without further purification, intermediate **5B** was dissolved in dry DCM (25mL) and treated with triethylamine (0.77mL, 5.5mmol) and $BF_3{\cdot}OEt_2$ (0.95mL, 7.7mmol) and stirred under N_2 overnight. The solvent was then removed *in vacuo* and the residue washed with copious H_2O to remove excess $BF_3{\cdot}OEt_2$. The solid was then dissolved in DCM (50mL) and washed with 1M NaOH (3x20mL) and H_2O (20mL). The organic layer was dried over $MgSO_4$, filtered and the solvent removed *in vacuo*. The crude product was purified by flash column chromatography (60:40 Hex:DCM (*v/v*)) to yield compound **6B** as a red-blue solid (336mg, 48%, two steps).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.5 Hz, $4H_d$), 7.96 (d, *J* = 8.0 Hz, $4H_b$), 7.30 (d, *J* = 8.0 Hz, $4H_a$), 7.12 (d, *J* = 8.5 Hz, $4H_e$), 6.99 (s, $2H_c$), 2.43 (s, $6H_f$).

^{13}C NMR (151 MHz, $CDCl_3$) δ 159.81, 145.65, 142.81, 141.79, 141.32, 132.37, 130.85, 129.77, 129.60, 129.45, 129.80, 119.46, 21.81.

^{19}F NMR (377 MHz, $CDCl_3$) δ -131.36 – -131.61 (m).

^{11}B NMR (128 MHz, $CDCl_3$) δ 0.95 (t, *J* = 38.0 Hz).

HRMS (ESI +ve) m/z: 608.2288, ($[M+H]^+$, $C_{34}H_{25}N_9BF_2$ requires 608.2293).

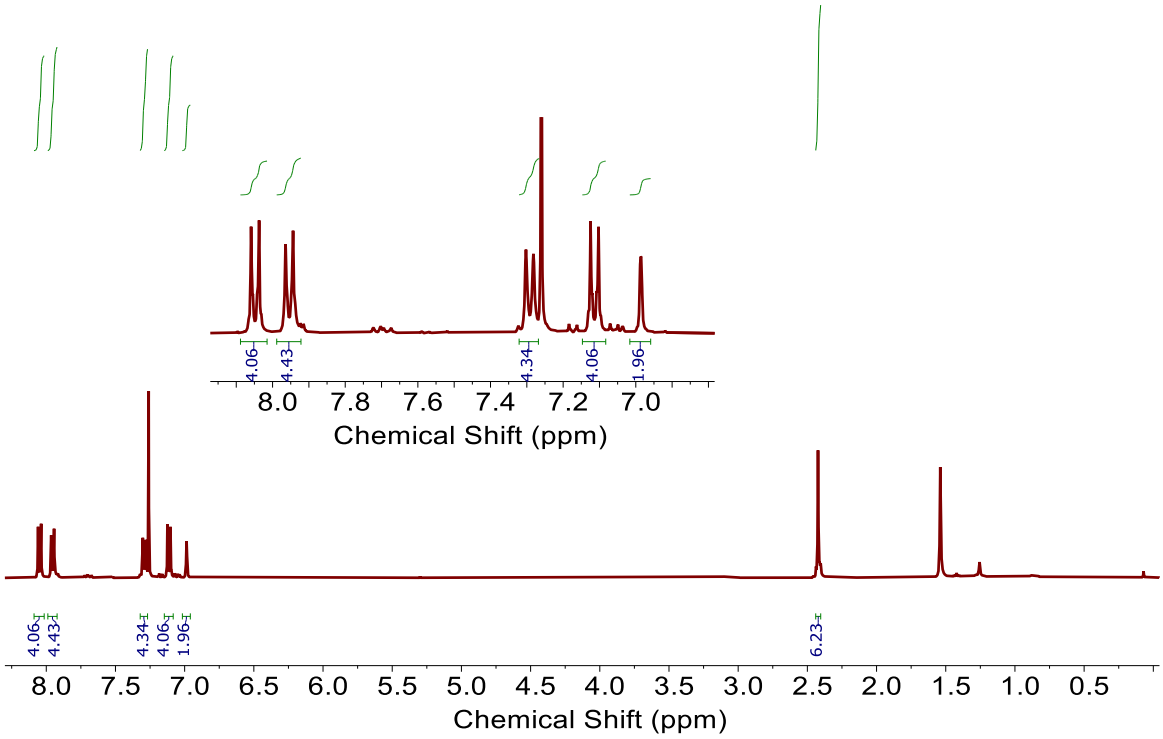


Figure S15. ^{1}H NMR spectrum of **6B.**

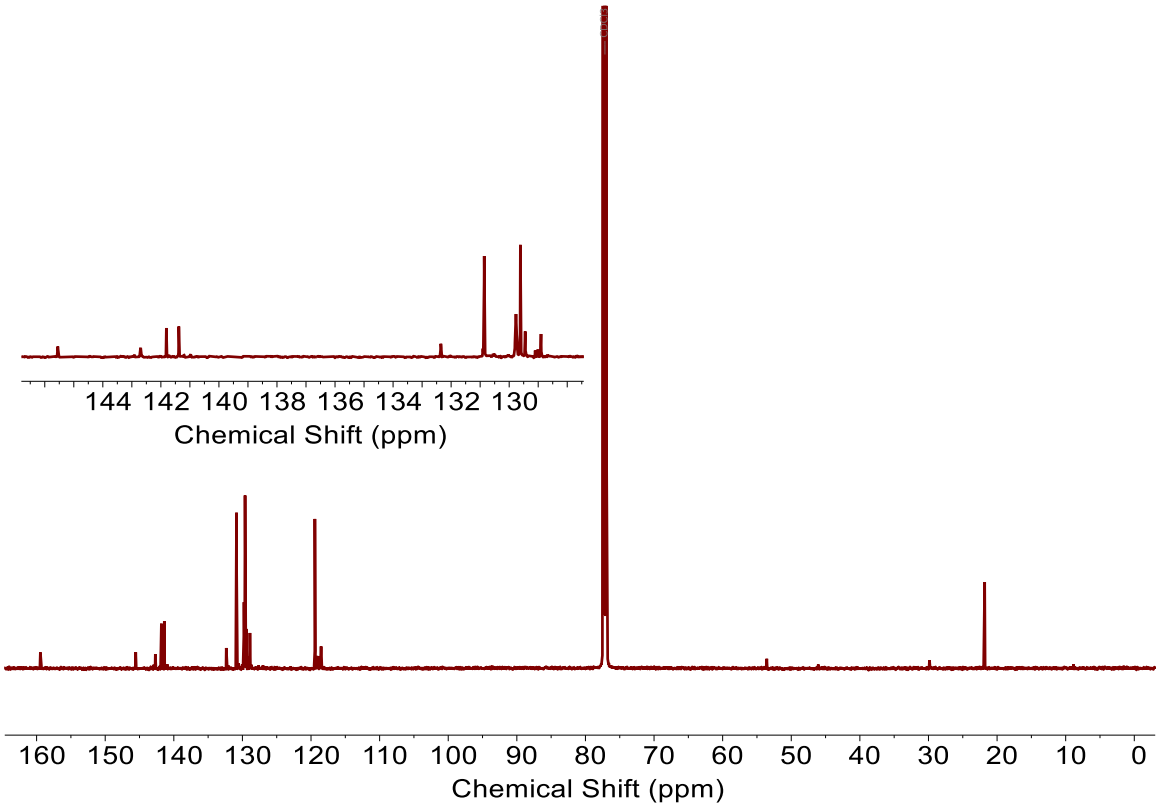


Figure S16. ^{13}C NMR spectrum of **6B.**

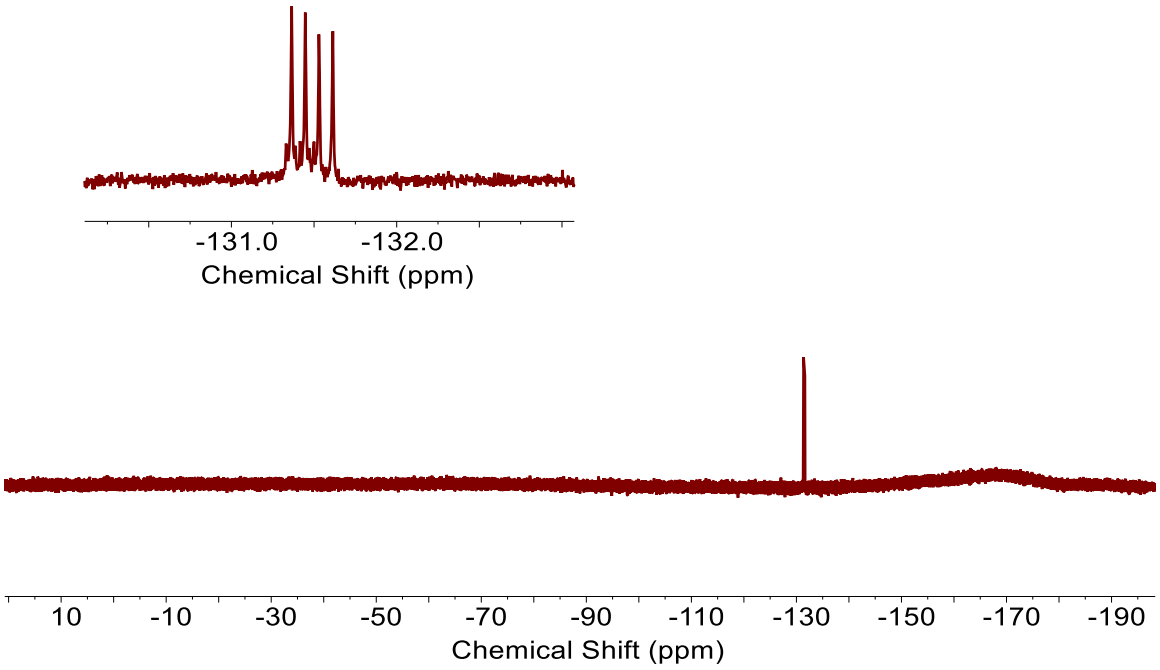


Figure S17. ^{19}F NMR spectrum of **6B.**

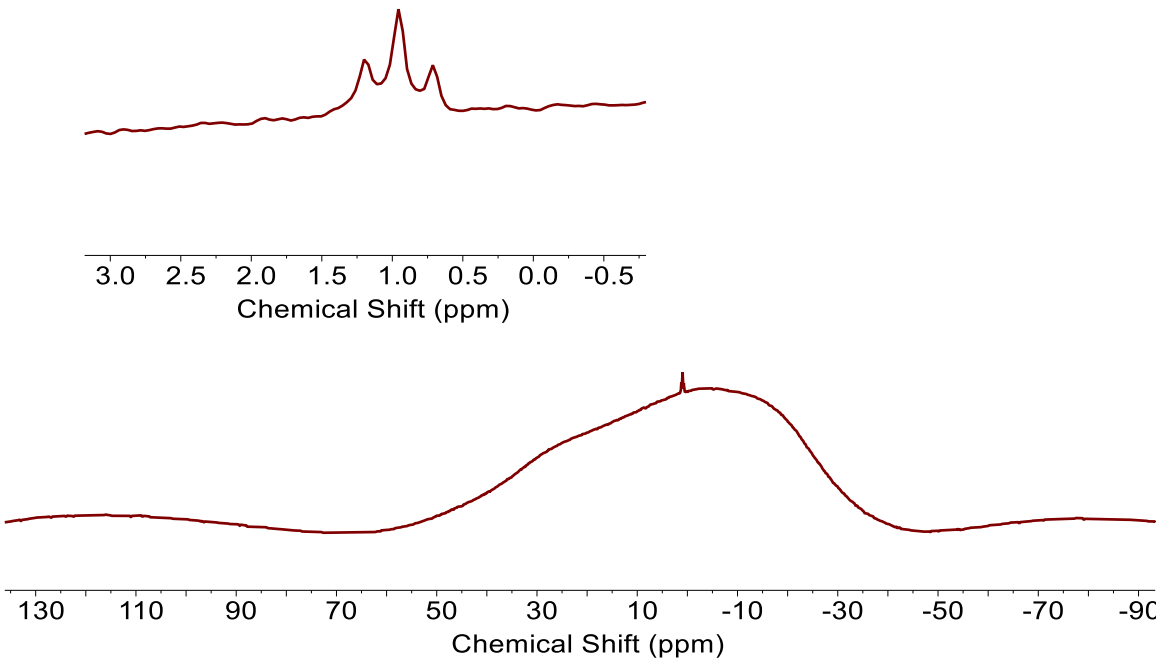


Figure S18. ^{11}B NMR spectrum of **6B.**

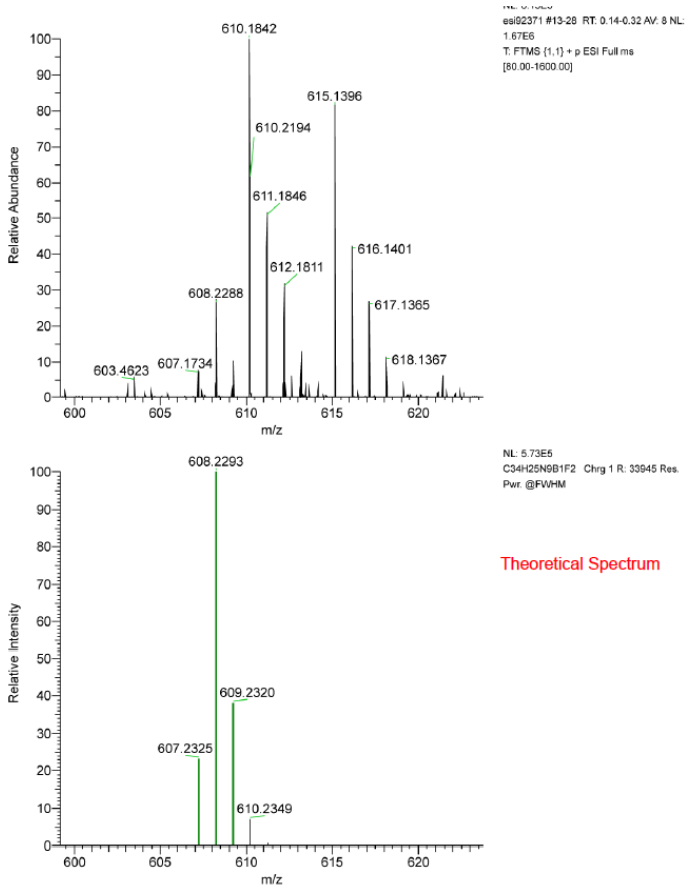
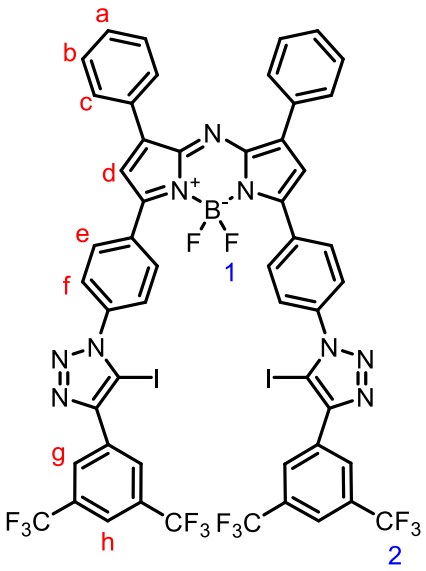


Figure S19. Experimental and theoretical mass spectra of **6B.**

Azide compounds frequently decompose in the mass spectrometer via loss of N_2,[5] leaving behind a reactive species, which may itself go on to form a variety of adducts. Therefore, the presence of additional peaks in the HRMS spectrum does not indicate the presence of impurities in the sample.

Receptor 1



Compound **6A** (45mg, 0.07mmol), 1-(iodoethynyl)-3,5-bis(trifluoromethyl)benzene[6] (**7**) (71mg, 0.173mmol), $[Cu(CH_3CN)_4]PF_6$ (7mg, 0.014mmol) and TBTA (9mg, 0.014mmol) were added to a microwave vial, which was flushed with N_2 for 10 minutes. Dry DCM (min) was added, and the mixture stirred at room temperature until TLC indicated consumption of the azide starting material. The reaction mixture was diluted with DCM (20mL) and washed with 0.1 M EDTA dissolved in aqueous 1M NH_4OH (10 mL) followed by water (10 ml). The organic phase was dried over $MgSO_4$, filtered, concentrated *in vacuo* and purified by flash column chromatography (50:50 DCM:Hex (*v/v*) to DCM) followed by preparative TLC (59:39:2 DCM:Hex:Acetone) to yield receptor **1** as a blue solid (37mg, 41%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (s, $4H_g$), 8.32 (d, J = 8.2 Hz, $4H_f$), 8.11 (d, J = 6.6 Hz, $4H_c$), 7.96 (s, $2H_h$), 7.77 (d, J = 8.2 Hz, $4H_e$), 7.51 (m, $6H_{a,b}$), 7.17 (s, $2H_d$).

^{19}F NMR (377 MHz, $CDCl_3$) δ -62.92(s, $12F_2$), -130.68 (m, $2F_1$).

^{11}B NMR (128 MHz, $CDCl_3$) δ 0.98 (t, J = 39.1 Hz).

Extremely low solubility prevented characterization by ^{13}C NMR.

HRMS (ESI -ve) m/z: 1307.0226, ($[M-H]^-$, $C_{52}H_{26}N_9BF_{14}I_2$ requires 1307.0284).

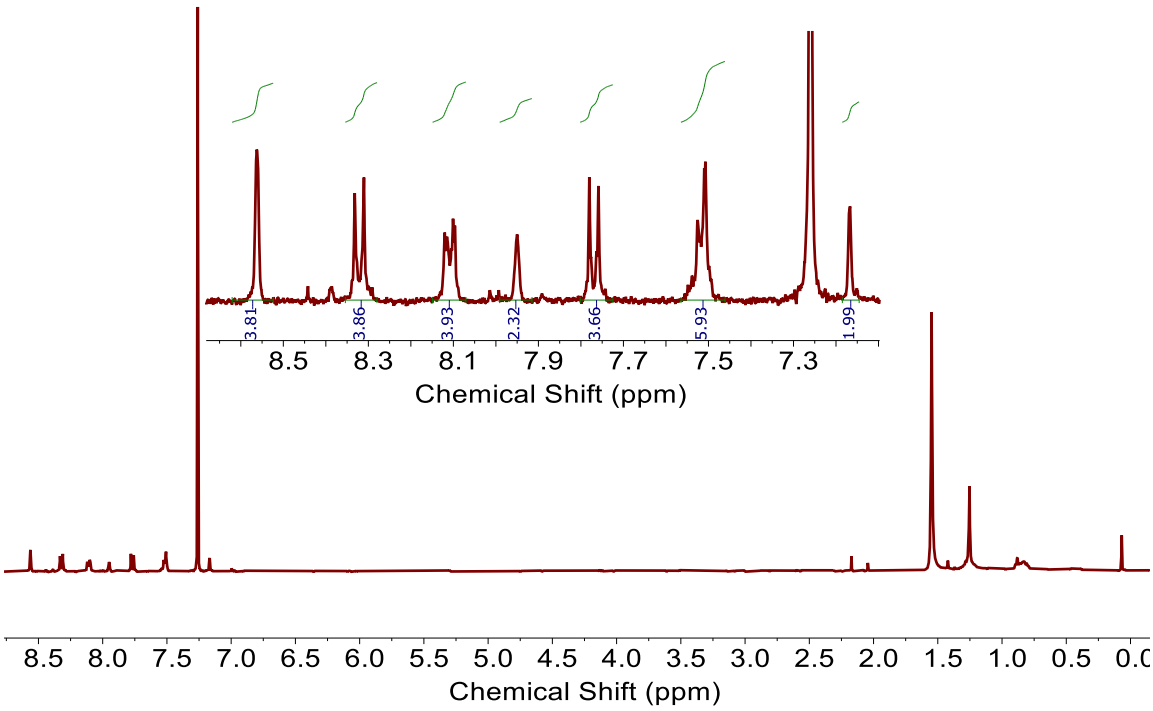


Figure S20. ^{1}H NMR spectrum of receptor **1.**

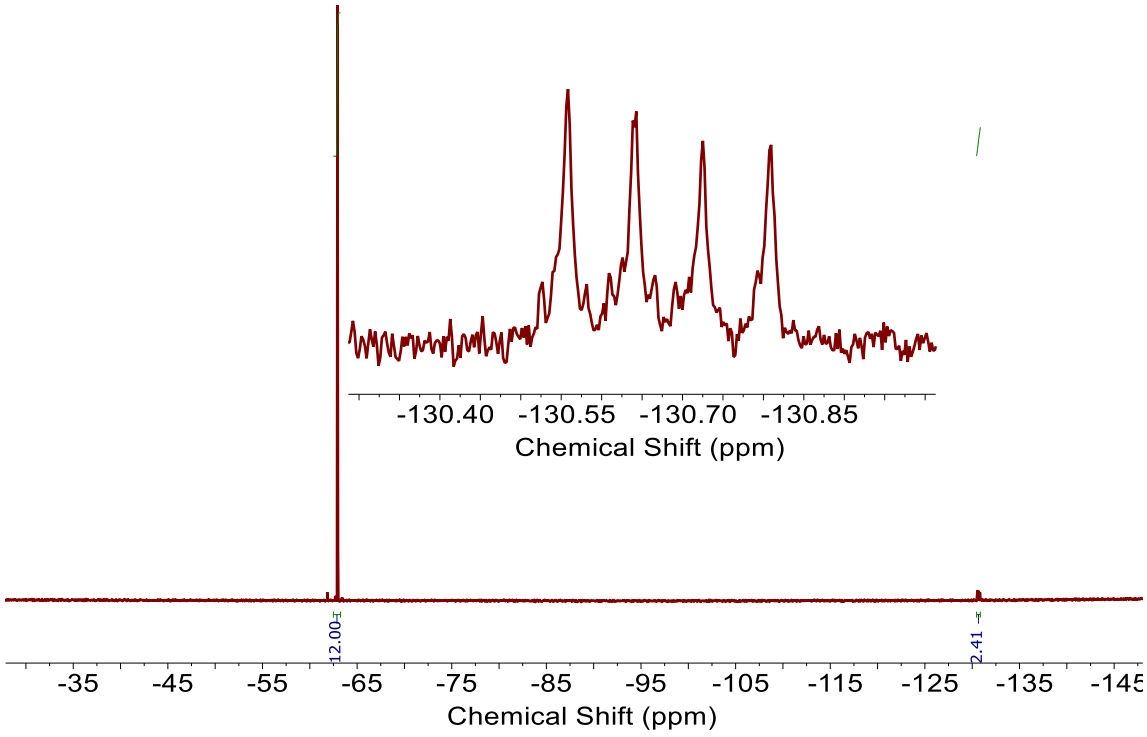


Figure S21. ^{19}F NMR spectrum of receptor **1.**

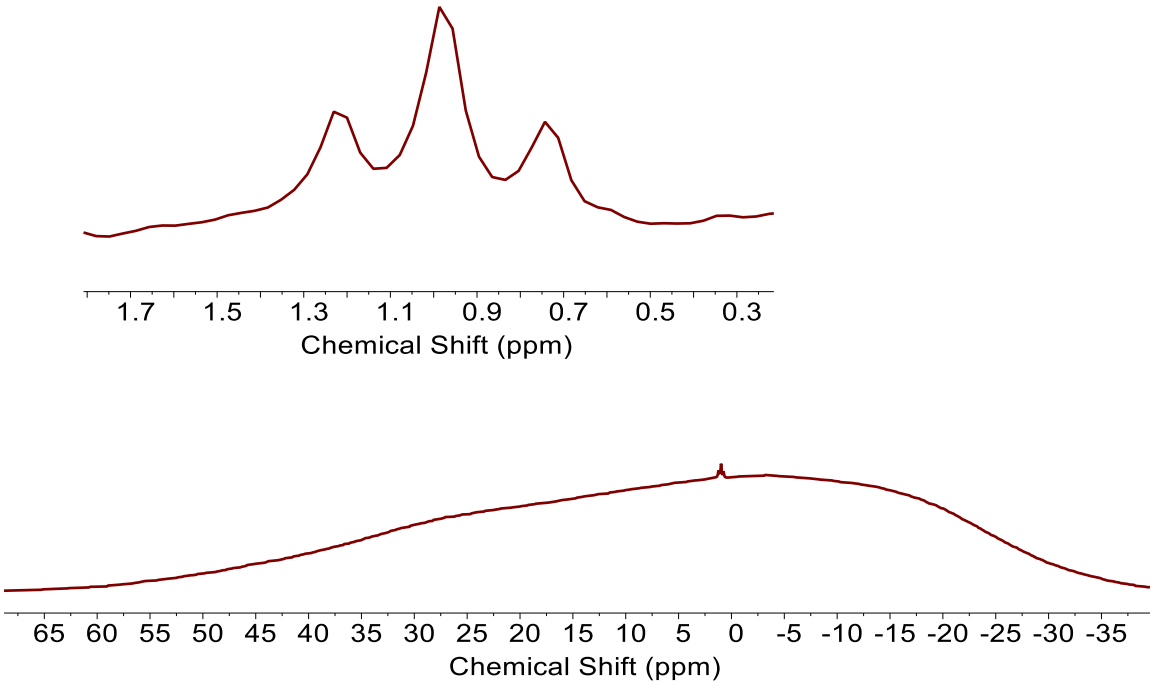


Figure S22. ^{11}B NMR spectrum of receptor **1.**

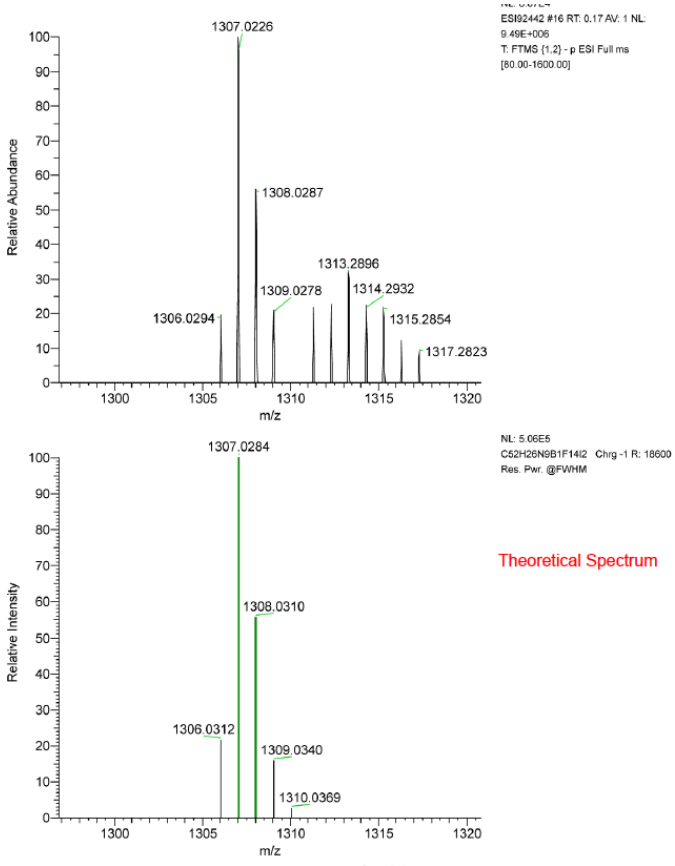
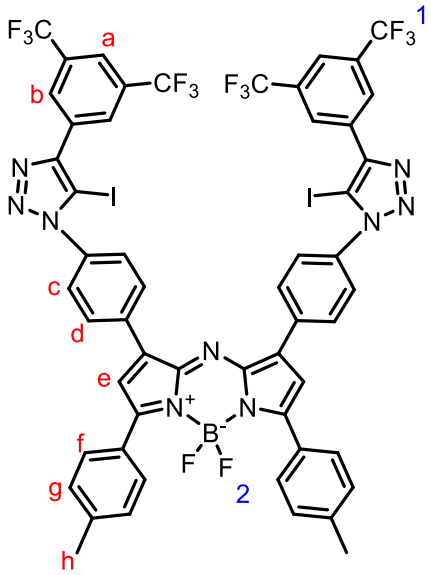


Figure S23. Experimental and theoretical mass spectra of receptor **1.**

Receptor 2



Compound **6B** (45mg, 0.07mmol), 1-(iodoethynyl)-3,5-bis(trifluoromethyl)benzene[6] (**7**) (71mg, 0.173mmol), $Cu(CH_3CN)_4PF_6$ (7mg, 0.014mmol) and TBTA (9mg, 0.014mmol) were added to a microwave vial, which was flushed with N_2 for 10 minutes. Dry DCM (min) was added, and the mixture stirred at room temperature until TLC indicated consumption of the azide starting material. The reaction mixture was diluted with DCM (20mL) and washed with 0.1 M EDTA dissolved in aqueous 1M NH_4OH (10 mL) followed by water (10 ml). The organic phase was dried over $MgSO_4$, filtered, concentrated *in vacuo* and purified by flash column chromatography (99.5:0.5 Toluene:EtOAc (*v/v*))) to yield receptor **2** as a green solid (52mg, 56%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (s, $4H_b$), 8.22 (d, *J* = 8.1 Hz, $4H_f$), 8.03 (d, *J* = 8.0 Hz, $4H_d$), 7.96 (s, $2H_a$), 7.73 (d, *J* = 8.0 Hz, $4H_c$), 7.35 (d, *J* = 8.1 Hz, $4H_g$), 7.17 (s, $2H_e$), 2.46 (s, $6H_h$).

^{19}F NMR (377 MHz, $CDCl_3$) δ -63.02 (s, $12F_1$), -132.04 (m, $2F_2$).

^{11}B NMR (128 MHz, $CDCl_3$) δ 1.08 (t, *J* = 36.0 Hz).

Extremely low solubility prevented characterization by ^{13}C NMR.

HRMS (ESI -ve) m/z: 1335.0542, ($[M-H]^-$, $C_{54}H_{30}N_9BF_{14}I_2$ requires 1335.0597).

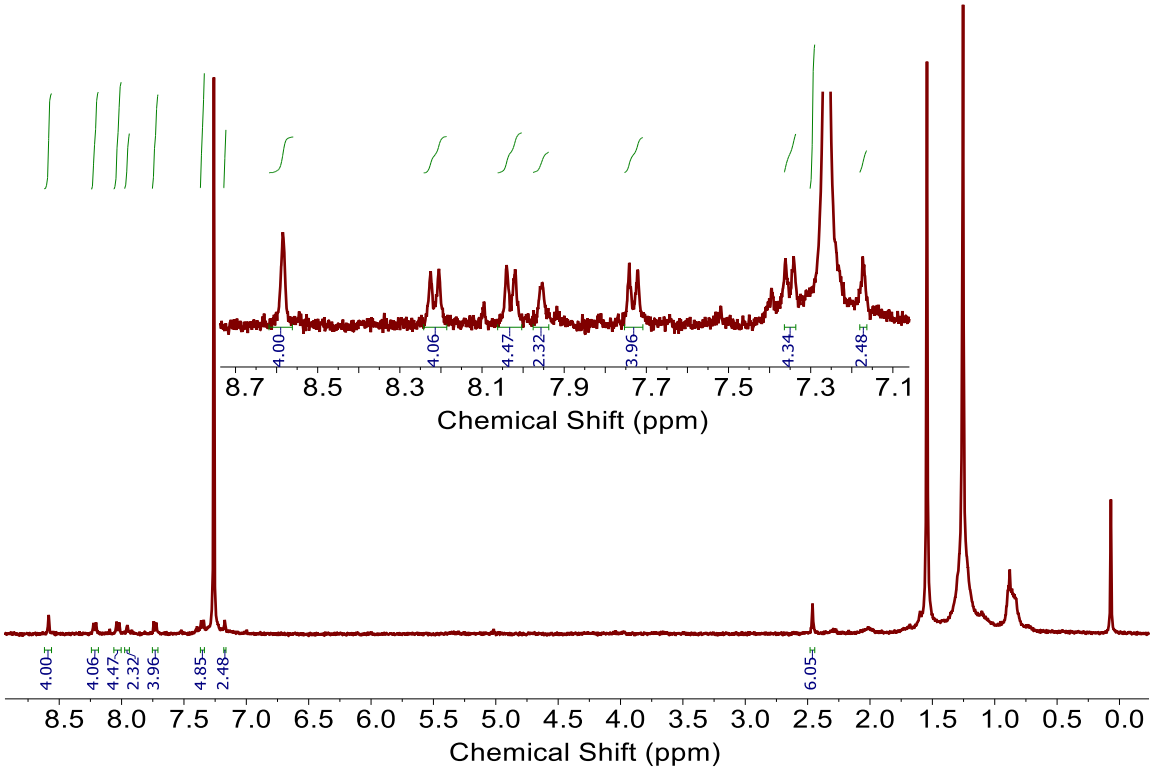


Figure S24. ^{1}H NMR spectrum of receptor **2.**

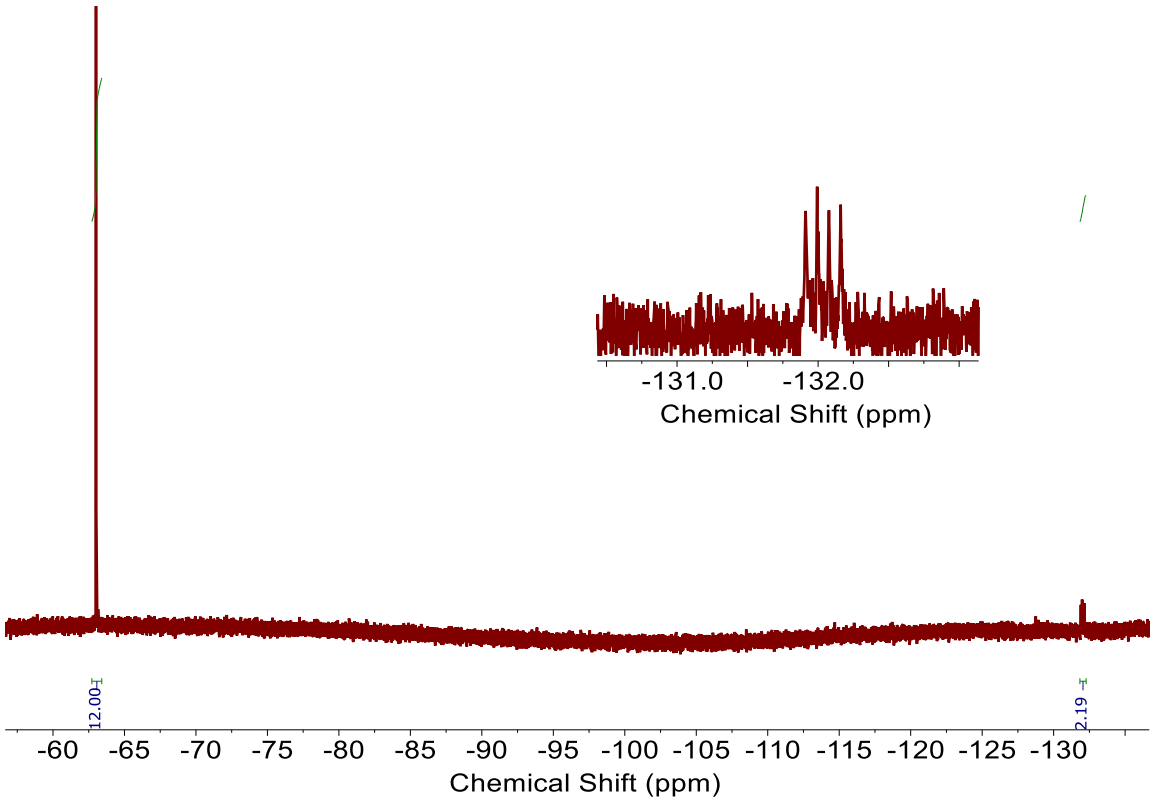


Figure S25. ^{19}F NMR spectrum of receptor **2.**

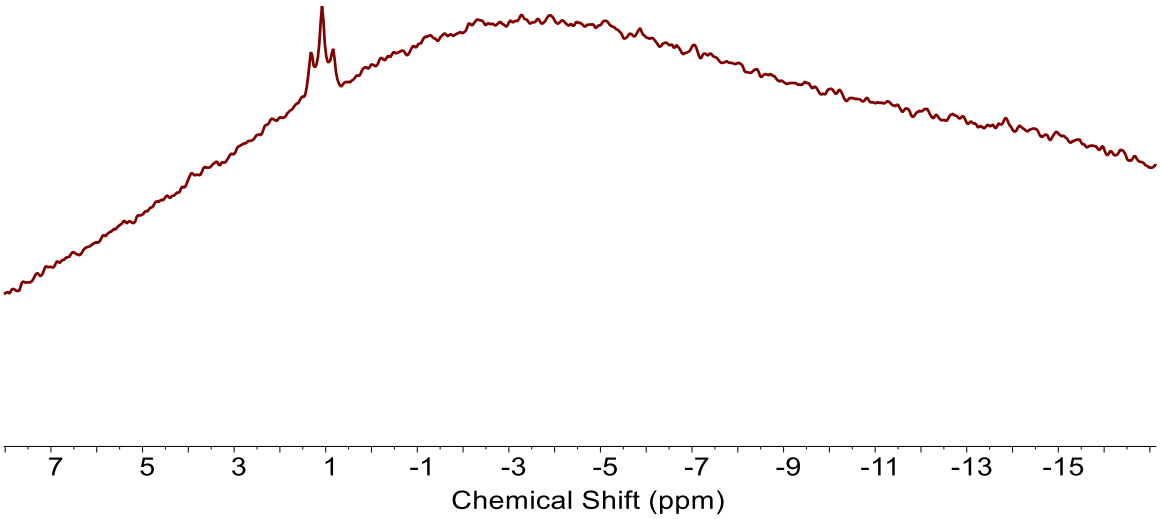


Figure S26. ^{11}B NMR spectrum of receptor **2.**

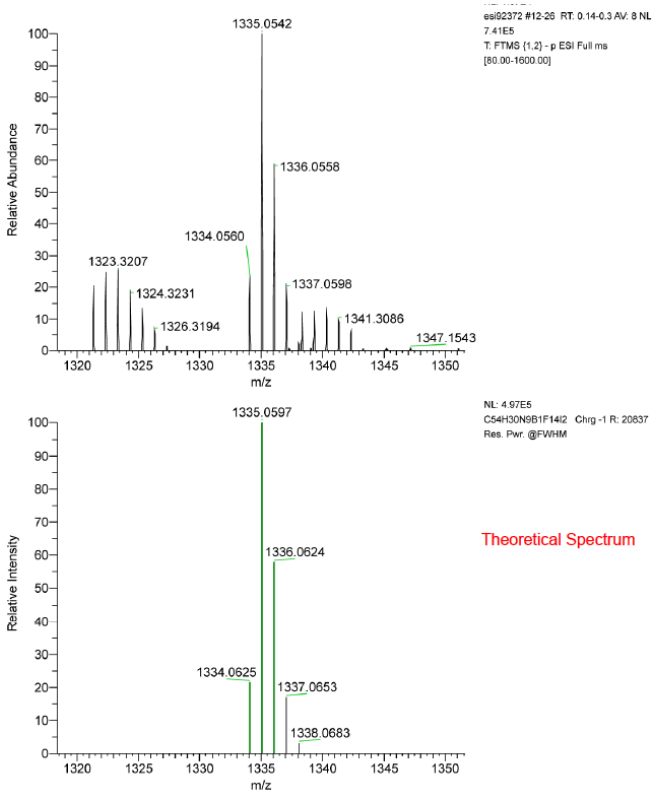


Figure S27. Experimental and theoretical mass spectra of receptor **2.**

3. Optical Characterisation of Receptors 1 and 2

The absorption and emission spectra for compounds receptors **1** and **2** are shown below.

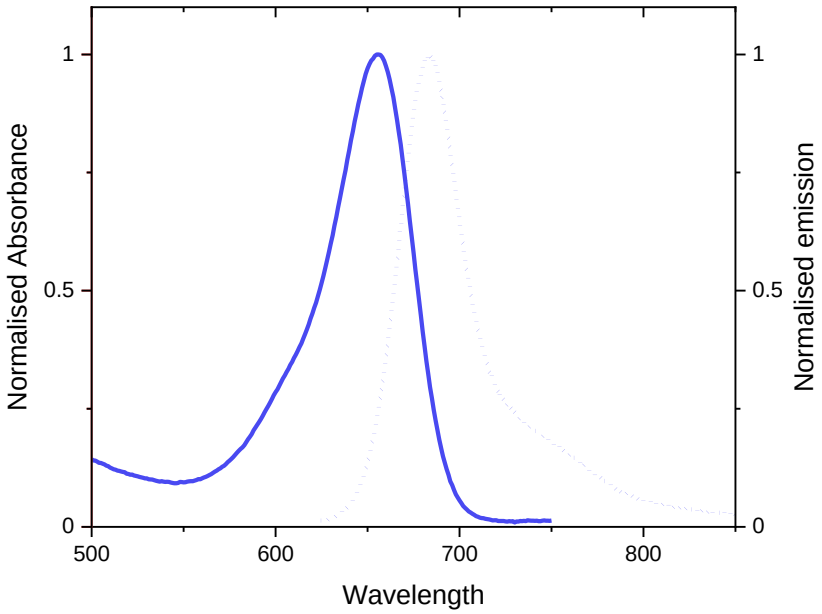


Figure S28. Absorption (solid) and emission (dotted) spectra of receptor **1.** (10 µM, acetone, 298K)

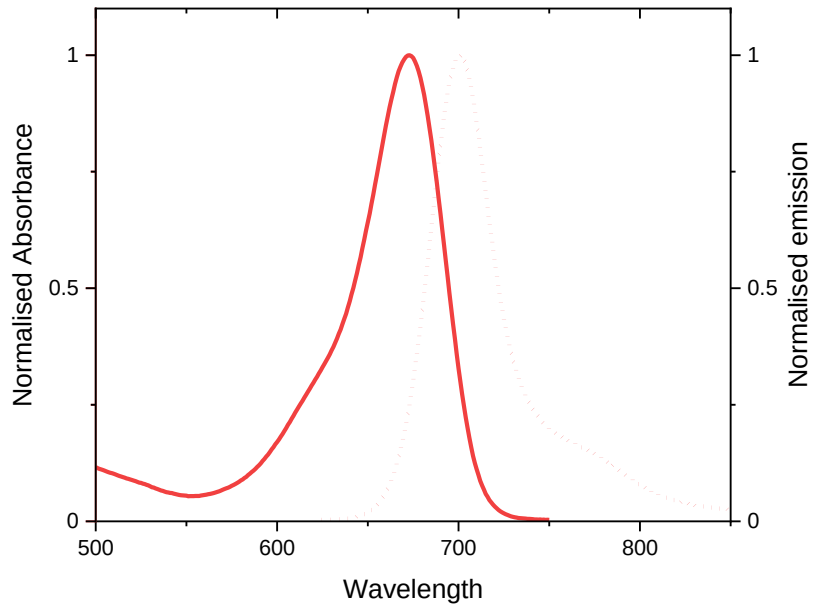


Figure S29. Absorption (solid) and emission (dotted) spectra of receptor **2.** (10 µM, acetone, 298K)

4. Fluorescence Titration Studies

As described in the main text, fluorescence titration studies of receptors **1** and **2** with TBAX (X = Cl, Br, I, HSO_4) salts were conducted in acetone. Representative, stacked emission spectra, with arrows showing the direction of change upon addition of analyte are shown below for receptor **2** (see main text for receptor **1**).

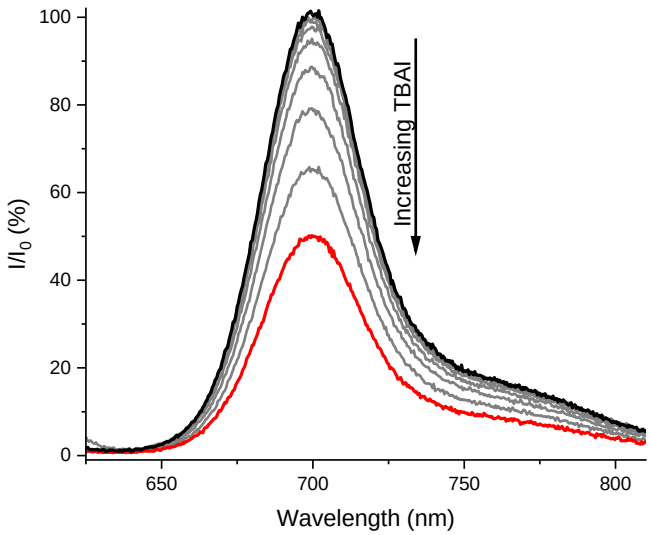


Figure S30. Stacked emission spectra of receptor **2** with increasing concentrations of I^- (up to a maximum of 2.8 mM), showing the directional fluorescence response. (1 µM, acetone, 298K)

In order to verify that the receptors remain responsive in the presence of water, fluorescence studies were conducted in 9:1 acetone/water in which fluorescence spectra was recorded in the presence and absence of excess TBACl (10 mM). These studies indicated that the receptors remain emissive in the presence of water (Figures S31-32). Addition of excess TBACl caused fluorescence quenching in both cases, demonstrating that the receptors remain sensitive to chloride (the halide with the highest hydration enthalpy) in the presence of water.

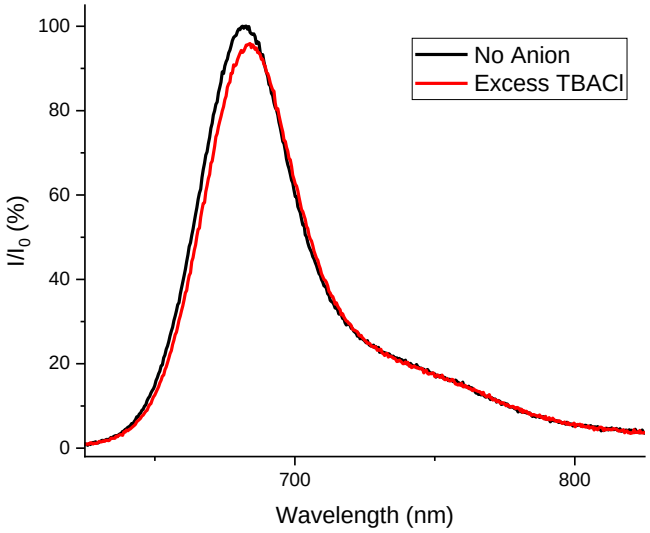


Figure S31. Stacked emission spectra of receptor **1** in the presence and absence of excess TBACl. (1 µM, 9:1 acetone/water (*v/v*), 298K)

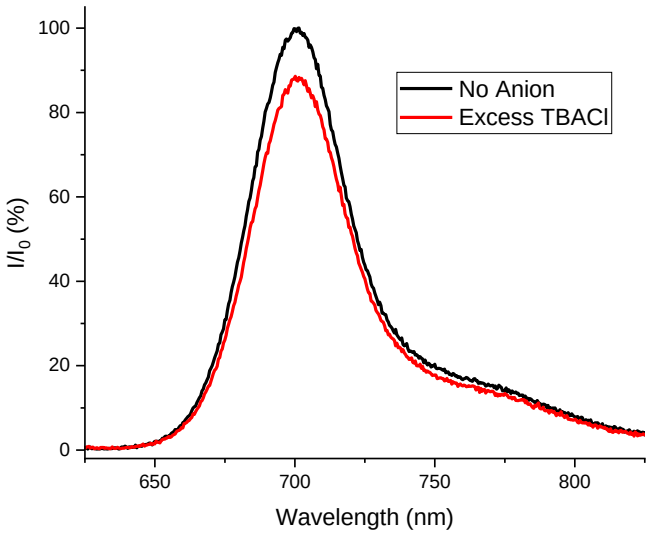


Figure S32. Stacked emission spectra of receptor **2** in the presence and absence of excess TBACl. (1 µM, 9:1 acetone/water (*v/v*), 298K)

5. Singlet Oxygen Generation Studies

In order to rule out any non-specific effects by which the presence of TBACl could influence the rate of singlet oxygen generation without binding to the aza-BODIPY fluorophore, control studies using compound **6A** were conducted.

An acetone solution containing compound **6A** (20 µM), DPBF (30 µM) was prepared and its absorbance spectra recorded before and after irradiation at 625 nm for 600 s. As shown in Figure S31, compound **6A** proved capable of generating singlet oxygen, with partial consumption of the DPBF $^1O_2$ trap after 600 s of irradiation at 625 nm observed.

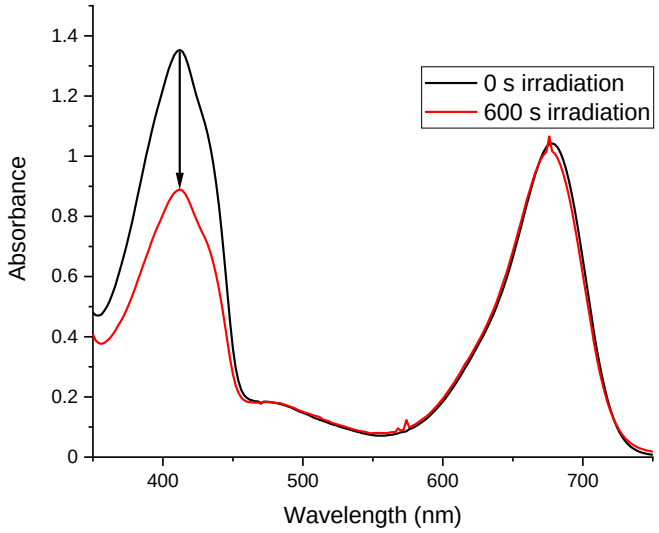


Figure S33. Absorbance of a solution initially containing DPBF (60 µM) and compound **6A** (40 µM), before and after 600 s irradiation at 625 nm. (Acetone, 298 K)

Subsequently, kinetic experiments were conducted in which acetone solutions containing either compound **6A** (40 µM), DPBF (60 µM) and TBACl (2 mM) or compound **6A** (40 µM) and DPBF (60 µM) were irradiated for 600 s and the rate of diminishment in absorbance at 410 nm was monitored (Figure S32).[‡] No significant difference in the rate of DPBF consumption was observed, indicating that the presence of TBACl has no effect on the rate at which compound **6A** generates $^1O_2$, and therefore suggesting that the observed rate difference for receptor **1** is caused by a specific Cl^- binding effect.

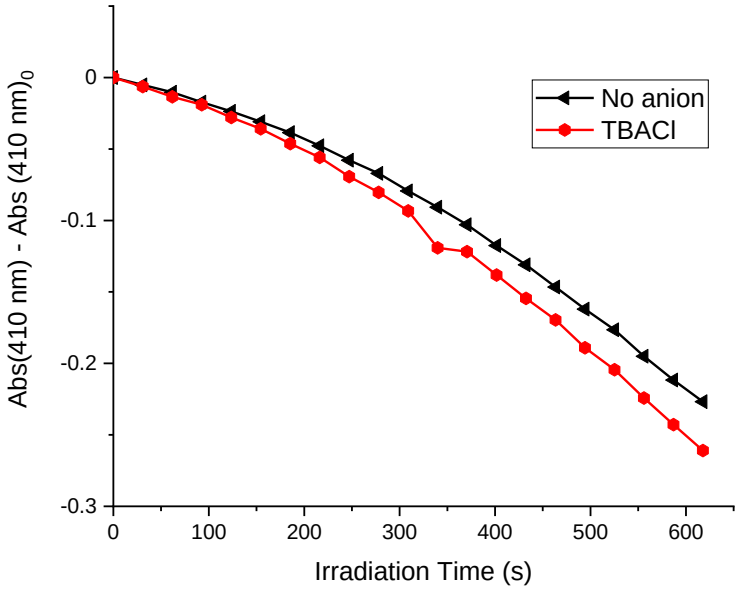


Figure S34. Plot of DPBF absorbance against irradiation time, in the presence and absence of TBACl. (Compound **6A**, acetone, 298 K)

Experiments to investigate the effect of the non-coordinating anion PF_6^- on the rate of $^1O_2$ production by receptor **1** were also conducted. Acetone solutions containing either compound **1** (20 µM), DPBF (30 µM) and $TBAPF_6$ (2 mM) or compound **1** (20 µM) and DPBF (30 µM) were irradiated for 600 s and the rate of diminishment in absorbance at 410 nm was monitored (Figure S33). Within the errors of the experiment, no significant difference (<5%) in the rate of DPBF consumption was observed, indicating that the presence of PF_6^-, does not significantly affect the rate of $^1O_2$ production by receptor **1**, ruling out non-specific effects.

The testing of other anions for their ability to also modulate the $^1O_2$ generation efficiency of receptor **1** was complicated by the known propensity of some commonly tested anions to react quickly with $^1O_2$ and other ROS, which would confound the results of any experiments. I^- is known to react with $^1O_2$,[7] and Br^- with other ROS such as $^{\bullet}OH$.[8] Other anions which are inert to reaction with $^1O_2$, such as ^-OAc, HSO_4^- and $H_2PO_4^-$ also proved unsuitable as they either did not elicit a fluorescence response from receptor **1** ($H_2PO_4^-$ and HSO_4^-, or caused decomposition of receptor **1** upon addition (^-OAc).

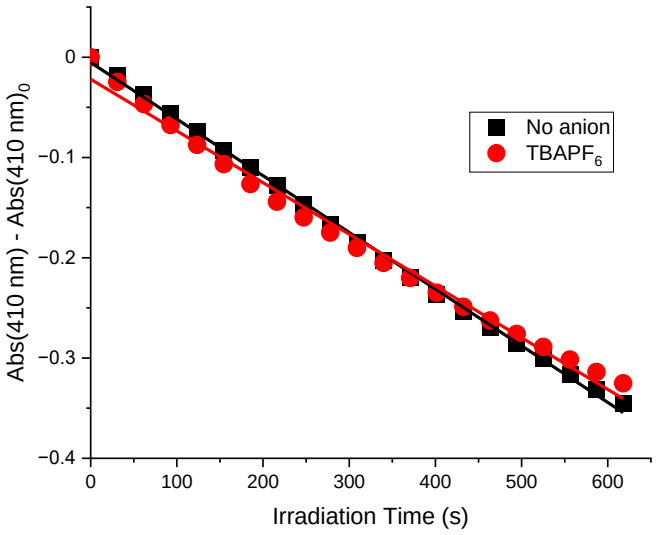


Figure S35. Plot of DPBF absorbance against irradiation time, in the presence and absence of $TBAPF_6$. (Compound **1**, acetone, 298 K)

The fluorescence quantum yield Φ_f (which is proportional to fluorescence intensity) is given by

$$\phi_f = k_f \times \tau_f = \frac{k_f}{k_f + k'} \qquad \text{(eqn. S1)}$$

where k_f is the rate of emission from the S_1 state and k' is the combined rate of all other, non-radiative decay processes from the S_1 state and τ_f is the fluorescence lifetime of the S_1 state. As the emission intensity of receptor **1** is diminished upon Cl^- binding, the fluorescence quantum yield in the presence of 2mM TBACl $\Phi_{f,\,Cl}$ is less than the fluorescence quantum yield in the absence TBACl $\Phi_{f,\,0}$:

$$\phi_{f,\ Cl} < \phi_{f,\ 0}$$ (eqn. S2)

Inserting the relation in eqn. S1:

$$k_{f,\ Cl} \times \tau_{f,\ Cl} < k_{f,\ 0} \times \tau_{f,\ 0}$$ (eqn. S3)

The lifetime measurements indicated that there is no significant change in fluorescence lifetime upon Cl^- binding: $\tau_{f,\ 0} = \tau_{f,\ Cl}$. Therefore:

$$k_{f,\ Cl} < k_{f,\ 0}$$ (eqn. S3)

The fluorescence lifetime τ_F is given by:

$$\tau_f = \frac{1}{k_f + k'}$$ (eqn. S5)

Therefore, as $\tau_{f,\ 0} = \tau_{f,\ Cl}$:

$$k_{f,\ Cl} + k'_{Cl} = k_{f,\ 0} + k'_0$$ (eqn. S6)

By inserting the relation in eqn. S3, we obtain:

$$k'_{Cl} > k'_0$$ (eqn. S7)

Showing that the rate of non-radiative decay pathways is increased by Cl^- binding for receptor **1**.

Notes and References

ǂ Deviations from linearity are due to the high concentrations of compound **6A** and DPBF required to observe significant DPBF quenching, because the $^1O_2$ generation efficiency of compound **6A** is worse than receptor **1**, as it does not contain any heavy atoms, such as iodine.

[1] Origin Corporation, **2023**.

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[8] J. Malešič, J. Kolar, M. Strlic, S. Polanc, *Acta Chimica Slovenica* **2005**, *53*, 450-456.